PHOSPHORUS REMOVAL BY CHEMICAL METHODS: SEPARATE AND COMBINED APPLICATIONS OF CALCIUM AND ALUMINUM SULFATES

Thesis for the Degree of M. S.
MICHIGAN STATE UNIVERSITY
James Raymond Plautz
1975

ABSTRACT

PHOSPHORUS REMOVAL BY CHEMICAL METHODS: SEPARATE AND COMBINED APPLICATIONS OF CALCIUM AND ALUMINUM SULFATES

By

James Raymond Plautz

While not a prophylactic measure, treating a lake with phosphate removing compounds is a therapeutic tactic for lake renewal. Combination and individual applications of calcium sulfate and aluminum sulfate were tested for their P-removal efficiency.

Each salt was tested at four initial pH levels (7.0, 8.0, 9.0 and 10.0) and in three different treatment concentrations: a. Al^{+3}: 20 mg/l; 15 mg/l; and 0.43 mg/l; b. $CaSO_4$: 25 mg/l; 35 mg/l; and 12.3 mg/l. A combined treatment of 12.3 mg $CaSO_4$/l and 0.43 mg Al/l was also tested at each initial pH level, but no combination of the former treatment dosages were applied.

Total and orthophosphorus removals on the order of 95 to 100% were observed for the higher aluminum doses, while the combined treatment removed 85% of the initial P over the four pH levels. A slight decrease (ca. 5 to 10%) in P-removal by aluminum was observed at pH 10.0 because the predominance of hydroxyl ion induces more rapid hydroxy-aluminum formation than hydroxy-aluminum-phosphate complexes.

Removal of phosphorus with $CaSO_4$ is less effective at all pH levels, with the majority (85%) of removal due to pH adjustment prior to treatment application. Interaction of phosphate with Ca^{+2} and $CaCO_3$ is a feasible explanation.

The combined treatment was ineffective in removing phosphate beyond that removed by initial pH adjustments. The calcium, alkalinity and pH fluctuations were identical to those of the pH control observations.

Aluminum appears to be more efficient and effective in removing phosphate than is calcium sulfate and is recommended for lake treatment rather than the calcium sulfate or combined applications.

PHOSPHORUS REMOVAL BY CHEMICAL METHODS: SEPARATE AND COMBINED APPLICATIONS OF CALCIUM AND ALUMINUM SULFATES

By

James Raymond Plautz

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Fisheries and Wildlife

1975

ACKNOWLEDGMENTS

I wish to extend my sincere appreciation to Dr. Eugene W. Roelofs for his patient guidance and encouragement throughout my degree program.

A sincere thank you is offered to Drs. Clarence D. McNabb, Jr. and Frank M. D'Itri for serving on my graduate committee as well as providing suggestions for completing this endeavor.

A special acknowledgment is due to Dr. Darrell King for the many hours of fruitful discussion which culminated in this research.

Jay Levine unselfishly assisted me in the laboratory for the greater portion of the study and I am thankful to him.

My fellow graduate students, especially Ted Batterson, did much to enrich the time spent here at Michigan State University.

My wife, Sharon, devotedly typed the rough draft of this thesis and patiently encouraged me during the period of study. I am grateful for all of her dedication.

This study was generously supported by an Environmental Protection Agency Grant (T 900331).

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Nutrient inactivation/precipitation is one of many methods employed for rehabilitating and maintaining natural lakes plagued by excessive nutrients and productivity. Numerous lakes and ponds in Europe and the United States are being treated with various substances including aluminum, calcium and zirconium as well as fly ash, powdered cement and aerobic lake muds (Dunst _et al_., 1974). Based upon Liebig's concept of a single nutrient limiting productivity, phosphorus (P) removal has proved to be the most feasible technological and economical method for reversing eutrophication of some waters.

This investigation was designed to evaluate combinations of calcium sulfate and alum (aluminum sulfate) for phosphorus removal from natural waters.

The effectiveness of aluminum, calcium and iron for P removal from municipal wastewater has been demonstrated and is an integral part of current wastewater treatment technology (Malhotra _et al_., 1964; Clesceri, 1968; Leckie and Stumm, 1970; Jenkins _et al_., 1971; Yuan and Hsu, 1971; Ferguson _et al_., 1973; and others). Extrapolation of these principles to natural lake systems involves several major differences between a natural lake and wastewater treatment. First is the magnitude of difference in wastewater P levels and amounts of coagulant added as compared to the lesser concentrations for lakes.

Secondly, wastewaters are manipulated chemically and physically to establish optimum conditions for P-removal, e.g., pH adjustment and residence time. Obviously, a lake or pond could not be subjected to such perturbations without catastrophic biological consequences. Thirdly is the amount of time for which treatment must be effective. Wastewater treatment with calcium and/or aluminum is completed within hours and the water passed on for further treatment or released as effluent. Successful treatment for lake rehabilitation requires not only the immediate effect of treatment, but also long term nutrient reduction at minimum financial and ecological cost.

Within the United States, the first such extension of wastewater technology for the treatment of an entire lake to remove P was at Horseshoe Lake, Wisconsin and began in May, 1970 (Peterson *et al.*, 1973). Their results showed an over-all improvement in the lake's condition as indicated by a decrease in total P, no large increase of total P within the anaerobic hypolimnion, the absence of algal blooms, and improved dissolved oxygen levels. Most notable was the absence of adverse ecological ramifications within the lake at alum concentrations of 200 mg/l (18 mg Al/l).

This research was based upon a lake rehabilitation method using Clean-Flo Lake Cleanser, a patented formulation of soluble calcium, aluminum and sodium cations designed to limit aquatic productivity by phosphorus removal (Lainge, 1974). Calcium and aluminum sulfates were used here to approximate this compound and their phosphorus removal capabilities were tested.

The dominant form of naturally occurring phosphorus is usually orthophosphate (PO_4^{-3}; HPO_4^{-2}; $H_2PO_4^{-1}$). These, and condensed anions of phosphate (e.g., $HP_3O_{10}^{-4}$), are capable of forming complexes, chelates and insoluble salts with several metal ions: $Ca^{+2} + H_2PO_4^{-1} = CaH_2PO_4^{+1}$; $Mg^{+} + HPO_4^{-2} = MgHPO_4$; $Fe^{+3} + H_2PO_4^{-} = FeH_2PO_4^{+2}$ (Sillen and Martell, 1964; Leckie and Stumm, 1970). The extent of such complexing is based upon the relative concentration of phosphate ion and metal ion, the pH as well as the presence of particulate matter and other ligands, such as sulfate, carbonate, flouride and organic species in the water. These processes also occur with condensed phosphates such as pyro- and tripolyphosphates (Stumm and Morgan, 1970; Jenkins _et_ _al_., 1971).

Chemical removal of phosphate is by precipitation, coagulation/flocculation and adsorption. These processes, discussed below in some detail, are based upon the strong tendency for chemical bonding between phosphate groups and metal ions (Stumm and Morgan, 1970).

Precipitation

Well defined reaction products are formed from simple orthophosphate and calcium or aluminum ions in aqueous solutions (Leckie and Stumm, 1970). Solid phase formation is predictable from equilibrium and solubility products (cf. Sillen and Martell, 1964; Stumm and Morgan, 1970) which suggest variscite ($AlPO_4 \cdot 2H_2O$) formation near pH 6.0. Between pH 7.5 and 8.5 and above pH 10.5, hydroxyaptite ($Ca_{10}(PO_4)_6(OH)_2$) is the calcium solid more readily formed. At high pH values (9.0 and above), calcite ($CaCO_3$) precipitation is in competition for Ca^{+2} with phosphate removal by calcium precipitation (Leckie and Stumm, 1970). However, P has recently been shown to coprecipitate with $CaCO_3$ (Otsuki and Wetzel, 1972) and, therefore, calcite precipitation may be synergistic to overall phosphate removal.

Phosphate removal efficiency of calcium generally increases with increasing pH, but hydroxyapatite formation requires a crystallization period before significant quantities of P are removed. This reaction is on the order of 60 to 120 days (Leckie and Stumm, 1970). Removal by $CaCO_3$ and $CaHPO_4$ formation are herein presented as plausible mechanisms for phosphate reduction with calcium.

Aluminum additions at neutral pH levels immediately (< 30 sec.) precipitate as Al-OH-P and Al-P compounds (Browman et al., 1973) with subsequent hydrolysis of the Al^{+3} to form polynuclear complexes. These require coagulation before P-removal is completed (Stumm and Morgan, 1962).

Coagulation/Flocculation

The following discussion draws mainly from two sources, O'Melia (1970) and Stumm and Morgan (1970). While O'Melia presents a generalized and fundamental review of coagulation and flocculation, Stumm and Morgan present more sophisticated and intricate aspects of the same processes.

The reactions of Al^{+3}, Fe^{+3} and Ca^{+2} with phosphate ions frequently result in colloidal dispersions resistant to settling. Coagulation reduces the phase stability and permits aggregation (flocculation) of the phosphate-metal ion complex (Leckie and Stumm, 1970).

Colloidal Properties. Solids in natural waters have electrically charged surfaces. Primary charge on a particle is fundamental to colloid stability and depends upon the nature of the solid as well as composition of the solution. Three principal processes are cited for the origin of the surface charge.

1. Chemical reactions at the surface. The ionization of certain functional groups at the particle surface results in a residual charge characterized by the degree of ionization. This proton transfer is, therefore, pH dependent with positive surface charges at low pH (high H^+) and negative surface charges at high pH (low H^+). There also exists for a particle a pH value at which the surface charge is zero. This pH is referred to as the zero point of charge (ZPC) or isoelectric point (IEP). Thus it may be stated that H^+ and OH^- are potential determining ions along with many others such as; carboxyl, amino and phosphate groups.

2. Lattice imperfections. Isomorphous replacements within the crystal lattice as well as lattice imperfections at the solid surface result in a charged framework (e.g., clays). Substitution of an Al^{+3} atom for a Si^{+4} atom in a solid SiO_2 tetrahedral array produces a net negative charge. The sign and magnitude of the charge produced by isomorphic replacements are independent of solution characteristics.

3. Preferential adsorption. The adsorption of specific ions on the particle surface also determines primary charge. Such adsorption is by hydrogen bonding, covalent bonding, and van der Waals' interactions. Electrostatic attraction may also augment ion adsorption.

The effects of ionization of surface groups or ion adsorption on primary charge are dependent upon characteristics of the aqueous phase whereas isomorphous replacement was not. This emphasizes the relationship between effective P removal by coagulation and ambient water characteristics (pH, temperature, etc.).

Electric Double Layer. This surface phenomenon exists at all solid-liquid interfaces in natural waters and results in interparticle repulsion which perpetuates colloidal dispersion. The double layer theory is the most widely accepted model of interfacial phenomenon significant in colloid destabilization.

The lack of a net electrical charge on colloidal dispersions (aqueous and solid phases together) is best explained by the Gouy-Chapman model of charge and potential distribution. Simply, it considers ions of opposite charge (counter ions) in the aqueous phase accumulating near the solid phase by coulombic attraction and repulsion forces. Due to thermal motion, the charge density and potential in the solution decreases rapidly with distance from the surface. Such a distribution results in particles with a diffuse layer of oppositely charged ions repulsed by the diffuse layer of another particle upon their interaction. Stability is inevitable.

Aggregation of particles necessitates destabilization of the colloid. The electric double layer theory asserts permanent or induced dipoles of the particles as the source of the attractive van der Waals' forces between particles. Induced dipoles occur as diffuse layers approach one another and the non-polar particle undergoes a degree of charge shift due to the adjacent electrical field. Particle parts reorient relative to the adjacent field allowing dipole interaction between atoms of the colloid. Strength of the induced dipole depends upon atom polarizability and the magnitude of the electrical field which in turn is a function of ionic strength of the aqueous phase. Increasing ionic strength of a solution decreases interparticle distance and results in compressing of the diffuse layer. This effectively decreases the magnitude of the energy of repulsion between particles, eliminates the potential energy barrier and destabilizes the colloid.

Adding a salt (indifferent electrolyte), such as $CaSO_4$ or alum, will compress the diffuse layer, lower the surface potential such that destabilization tends to occur and allow particle flocculation. Coagulation with aluminum may involve principles from a second theory in combination with the above.

Chemical Bridging Model. The previous discussion of the sources of primary charges on particles emphasized the ability of solids in solution to reach stable conditions by electrostatic repulsion and is the point from which chemical bridging will be explained. The electric double layer model used electrolyte additions for destabilization; chemical bridging is based upon the action of polyelectrolytes or polymers.

Natural and synthetic macromolecules have been successfully used for coagulation. Simply stated, a polymer molecule can attach to a particle surface at one or more adsorption sites with the rest of the polymer extending into the solution and capable of adsorbing to vacant sites on another colloidal particle (bridging). Restabilization of the colloid occurs when the extended portion adsorbs to vacant sites on the original surface. Adsorption of anionic polymers on negative surfaces is common as explained by Stumm and Morgan (1970). With opposite charges on particle and polymer, attraction is postulated to be coulombic with the concession that other chemical forces outweigh electrostatic interactions.

Differing conclusions as to why the colloids destabilize in the presence of polymers are presented, but, from the literature, no definitive conclusions were apparent (Stumm and Morgan, 1962; O'Melia, 1969; Stumm and Morgan, 1970). Optimum destabilization occurs with polymers of charge similar to that of the colloid surfaces and when adsorption sites are only partially filled. Complications arise when the added polymer saturates available surfaces (overdose), or agitation breaks polymer-surface bonds, usually resulting in restabilization of the colloid and an ineffective treatment. Water purification and wastewater treatment employ the "Dow Process", a method using Fe^{+3} followed by a polyelectrolyte coagulent for phosphorus removal, which functions according to the chemical bridge theory (Jenkins _et al_., 1971).

Coagulation with Aluminum. All metal cations in water are hydrated, therefore coagulation is brought about by metal ion hydrolysis species (e.g., $Al(OH)_3$) and not by free, multivalent metal ions. The amphoteric properties of these hydrous oxides, due to the metal hydrolysis reaction, further support H^+ and OH^- as potential determining ions of the hydrous oxide precipitate. These hydrous oxides may also be considered polyelectrolytes and fit the chemical bridge model, but are technically chelators with hydroxyl as the ligand.

There is also a strong tendency for these hydroxides to react with anions and cations. Anion reactions predominate at pH values below the isoelectric point (IEP) while above the IEP more OH^- ions are coordinated, facilitating cation interaction (Stumm and Morgan, 1970).

Hydrolyzed metal ions are strongly adsorbed at solid-solution interfaces, but a definitive theory for its explanation is not yet available. The presence of the coordinated OH^- group is highly significant and may render the adsorbed complex more hydrophobic. This may, in turn, enhance covalent bond formation between metal atoms and the solid surface (Stumm and Morgan, 1970).

The hydrolysis reactions of aluminum are more complicated than those of Fe^{+3}, but the aluminum salts are more easily hydrolized. A stepwise hydrolysis of Al^{+3} to $Al(OH)_4^{-1}$ is pH dependent and various intermediates have been postulated. Formation of poly-nuclear ionic aluminum hydroxo complexes such as $(Al_6(OH)_{15})^{+3}$ (aq.) have been substantiated, but the main hydrolysis product is a complex with a 2.5-1 OH^- to Al^{+3} stoichiometric molar ratio (Stumm and Morgan, 1962). O'Melia and Stumm (1967) have shown destabilization of colloidal dispersions by such soluble, polymeric kinetic intermediates.

Flocculation. This second step in solids removal is concerned with particle transport theories which are based upon the fluid and particle mechanics required for particle contact and an in-depth description is irrelevant. The degree of aggregation of the destabilized colloid particles is determined by the amount of contact between particles. Kinetic flocculation is described in terms of particle transport and may be orthokinetic or perikinetic. Orthokinetic flocculation is brought about by fluid motion or agitation and increases particle contact by an energy input. Perikinetic flocculation occurs by Brownian diffusion, is unaffected by fluid agitation and thereby augments orthokinetics; especially with particles less than one micron in size.

Lake treatment employs the orthokinetic principles by means of the method of coagulant application, usually in a slurry with mixing provided by the boat motor. Likewise, the experimental methodology describes treatment application aided by a magnetic stirrer.

Bioflocculation. The tendency for bacteria and algae to adhere to interfaces and each other (Stumm and Morgan, 1970) is not insignificant relative to phosphate removal. Pavoni and coworkers (1971, 1972) have presented evidence demonstrating the production of exocellular polymers during the endogenous (declining) phase of growth as well as the role of these polymers in an aggregating interaction. The removal of inorganic kaolinite and silica dispersions from solution was also effected by exocellular polymers.

These long chains of organic compounds, generally categorized as polysaccharides, proteins, RNA and DNA, are characteristically of negative charge and capable of flocculation by a bridging mechanism based upon electrostatic or physical bonding (Stumm and Morgan, 1970; Pavoni *et al*., 1971, 1972).

That phytoplankton release dissolved organic matter is well supported by the literature (cf. Wetzel, 1975). Because the nature of these exocellular compounds is such that particle aggregation results, their role in phosphate removal, whether inadvertant or determinant, is certainly contributory and must be considered.

Adsorption

The previously discussed methods of P removal, precipitation and coagulation/flocculation, are characterized by different types of "sorption" phenomenon in that adsorption of phosphates on ferric or aluminum oxides or hydroxides results from the same chemical forces which form complex ions or insoluble salts. Precipitation then, becomes a special case of adsorption wherein surface metal ions react with solution species to form metal ion-phosphate bonds (Stumm and Morgan, 1970).

Polyphosphate adsorption onto clay plate edges has been described by chemisorption in which Al^{+3} ions at the edges specifically interact with the solution phase phosphate (Van Olphen, 1963).

Stumm and Morgan (1970) describe adsorption as involving three steps when a solute molecule is adsorbed on the surface of a solid: 1) The solute molecule is removed from the solution; 2) The solvent is removed from the solid surface with; 3) the subsequent attachment of solute to the surface. Energy for the adsorption process may be obtained from chemical interactions, such as covalent bonding, from electrostatic interactions (e.g., ion exchange reactions) from van der Waals' attraction, from hydrogen bonding, or from orientation energies. The affinity of the aqueous solvent for the solute may prevent solute-solid adsorption, while on the other hand, adsorption may occur against the electrostatic repulsion of like charges on the solid surface and solute. Large organic ions and organic dipoles are preferentially adsorbed at the interface due to the low affinity of hydrocarbons for the aqueous phase.

It may be understood from the above that phosphorus, and especially phosphate, can become attached to solid phases in solution. If particle density, solution viscosity and temperature are appropriate, settling will occur naturally; however, as pointed out previously, the tendency is for such particles to remain suspended or settle very slowly. Such situations require ammendments which facilitate removal.

Hydrolysis of aluminum in water leads to formation of hydroxyl bridging between colloid particles and concomitant aggregation. As this floc settles through the water column, adsorption to and physical entrapment by the floc probably occurs. This represents the combined action of surface phenomenon and physical methods of removal.

Summary

Phosphate removal with $CaSO_4$ and alum is based upon precipitation and adsorption mechanisms. While mainly the surface phenomena of electrostatic forces are involved, evidence also supports physical entrapment of particles within the settling floc or surface adsorption on precipitated aggregates.

The following information was collected from a laboratory investigation of several treatment levels of the respective compounds at various pH levels. In an attempt to demonstrate each "salt's" ability to remove phosphate from water, they were applied separately. Culmination of the investigation was in their combined application. Observed removal corresponds well to the foregoing information.

METHODOLOGY

The evaluation of aluminum (Al) and calcium sulfate ($CaSO_4$) in removing phosphorus (P) from natural waters was conducted for three treatment levels and at four pH values. *In situ* P concentrations of the water were unaltered.

Experimental Units

Three successive experiments were conducted within a three month period. For each experiment, hereafter referred to as Exp. I, Exp. II and Exp. III, four 5-gallon (17 liter) Nalgene carboys were filled at the Water Quality Management Project located on a southern portion of the Michigan State University campus. Consisting of a series of four flow-through ponds, this project effects tertiary treatment on secondary effluent pumped directly from the East Lansing sewage treatment plant.

In order to have experimental phosphorus levels comparable to a naturally eutrophic lake, water for Exp. I and Exp. II was taken from Pond 1. Because of continual wastewater inputs to Pond 1, phosphorus concentrations exceeded those used in Exp. I and Exp. II so water for Exp. III was collected from Pond 2. Temperature and pH were recorded in the field for each water collection.

At the laboratory, portions of the water were set aside for subsequent chemical analysis, while the remainder was distributed, by two-liter volumes, into 26 covered Erlenmeyer flasks. Treatment was applied following a 24-hour equilibration period.

Treatment Application

Calcium sulfate ($CaSO_4 \cdot 2H_2O$) and alum ($Al_2(SO_4)_3 \cdot 18H_2O$) were weighed into plastic trays prior to each experiment (Table 1). The combination in Exp. III was composed of the relative proportions, shown in Table 1, and homogenized by mortar and pestle prior to weighing the treatment amounts.

Levels of pH 7.0, 8.0, 9.0, and 10.0 were adjusted with sodium hydroxide and hydrochloric acid immediately before the respective compound was added. Inadvertantly, sulfuric acid was used during Exp. I but, as compared to succeeding experiments, no apparent effect was detectable. To facilitate rapid pH adjustment and treatment, a magnetic stirrer was used throughout both treatment steps.

To simulate treatment application in slurry form, an aliquot of water was withdrawn from the flask, added to the weigh-tray of compound and stirred. The mixture was poured into the flask and the weigh-tray rinsed with deionized-distilled water (less than 1 ml). Rapid mixing at a higher speed continued for approximately 45 seconds thus completing the treatment process, in an average of 258 seconds per flask.

Two types of controls were included for each treatment. Control flasks for each pH were established by adding only acid or base to reach the desired pH. Ambient controls were those flasks to which no alterations or adjustments were made.

Table 1. Weights (mg/l) of calcium sulfate and aluminum sulfate applied for each of three experiments. Aluminum equivalent in parenthesis.

Experiment	$CaSO_4 \cdot 2H_2O$ mg/l	$Al_2(SO_4)_3 \cdot 18H_2O$ mg/l	Combined mg/l
I	25.0	493.8 (20.0)	--
II	35.0	370.4 (15.0)	--
III	12.3	2.7 (0.43)	15

Exp. I and Exp. II each had a total of 8 flasks as pH controls, 8 as $CaSO_4$ units, 8 as alum units, and 2 ambient controls. Exp. III was run with 8 pH controls, 8 with the combined treatment, 4 with alum only (pH 8 and 10), 4 with $CaSO_4$ only (pH 8 and 10), and two ambient controls. Replication at each of the four pH levels was in duplicate.

Sampling

Samples were collected at various times over a 96-hour observation period as shown in Table 2. Only the 48-hour samples were analyzed for all parameters in each experiment and thus the following data are values from the 48-hour samples. Time zero is the midpoint of treatment application.

Water was drawn from a mid-depth of each flask, well above any settled matter present. Subsequent sampling from each flask attempted to draw from the same mid-depth from which the first sample was collected. To minimize sampling time, a vacuum pump and tygon tubing were used to collect the water into 500-ml Nalgene bottles. Collected samples were held at $0^{\circ}C$ until analysis (< 2 days) and no preservatives were added.

Total and orthophosphorus samples, except those at 24 and 48 hours, were drawn by transfer pipet from each flask and immediately analyzed.

Analytical Methods

All chemical analysis were performed to specifications outlined in Standard Methods for the Examination of Water and Wastewater (APHA˙ *et al.*, 1973) and included alkalinity, hardness, temperature, pH, and phosphorus.

Table 2. Table of sampling frequency of chemical analysis for Exp. I, II, III.

	Hours Post Treatment									
Analyzed	1	4	7	9	24	36	48	72	84	96
All parameters					II, III	I	I, II, III			
Total P	II		II	II	II, III	I	I, II, III			
Ortho P	II	III	II	II	II, III	I	I, II, III	II	I	I, II, III

Total alkalinity was to pH 4.5 with bromcresol green-methyl red indicator. Calcium and total hardness were analyzed with Hach prepared reagents and titrant. The pH for both laboratory and field was determined with a Chem-Mate meter and combination electrode while a mercury thermometer was used for temperature. Phosphorus colorimetry was by the ascorbic acid-single reagent method and absorbance read at 880 nm on a Bausch and Lomb Spectronic-20.

Total P digestion by persulfate oxidation was carried out in 125-ml Erlenmeyer flasks and boiled on a hot plate. Following cooling and neutralization (pH 7.3) each sample was rediluted to the original 100-ml volume.

Orthophosphate values represent that portion of the total P in 20 ml of untreated water which will react with the combined reagent after ten, but not more than thirty minutes following its addition to the sample. Prior to adding the combined reagent, 1.0 ml of 2-propanol was added to each sample.

Glassware for phosphorus analysis was cleaned with a sulfuric acid-dichromate solution, rinsed and washed a second time with hot, 30% (v/v) HCl followed by triple rinses of deionized-distilled water. All other glassware was cleaned by the same procedure, but without the hot HCl.

RESULTS AND DISCUSSION

In considering the following data, it will become obvious that pH adjustment confounds the direct determination of a treatment effect. Also in this regard is the limited scope of effective extrapolation from the laboratory to the field.

The data will be considered from several aspects: 1) effect of pH adjustment; 2) effect of calcium sulfate treatment; and, 3) effect of aluminum treatment. Each of these aspects are related to changes in the alkalinity, pH, calcium, ortho and total phosphorus. Each compound is further described in terms of its contribution to P-removal by the combined treatment.

Effect of Adjusting pH

To provide information on changes induced by adjusting the pH prior to treatment application, each experiment included eight units referred to as pH controls.

Table 3 lists the initial, or pre-treatment, values for the parameters measured throughout each of the three experiments. Changes occurred in the five parameters due to pH adjustments alone. Table 4 presents data collected 48-hours after the pH was initially set. Each value is the mean of four separate determinations; two within each flask of the duplicated units (cf. methods section). In other

Table 3. Measured values of five parameters prior to initial pH adjustment for the three experiments.

Parameter	Exp. I	Adjusted pH Exp. II	Exp. III
Alkalinity (meq/l)	2.3	3.3	2.2
pH	7.8	7.2	9.4
Calcium (mg/l)	64.6	72.8	58.4
Ortho-P (mg/l)	0.240	0.332	0.128
Total-P (mg/l)	0.266	0.414	0.155

Table 4. The effect of adjusting pH on five parameters 48 hours after the adjustment.

Parameter	Adjusted pH 7.0 I	II	III	8.0 I	II	III	9.0 I	II	III	10.0 I	II	III
Alkalinity (meq/l)	1.8	2.3	1.3	2.1	2.8	1.7	2.1	2.9	2.1	1.8	3.2	2.2
pH	7.1	7.4	7.3	7.7	8.2	8.0	7.6	8.3	9.2	9.3	10.3	10.1
Calcium (mg/l)	58.5	67.2	53.8	55.6	76.6	52.4	49.4	62.6	58.7	8.4	21.8	40.2
Ortho-P (mg/l)	0.222	0.272	0.126	0.234	0.300	0.124	0.216	0.300	0.132	0.035	0.044	0.124
Total-P (mg/l)	0.260	0.382	0.174	0.286	0.356	0.176	0.254	0.350	0.190	0.062	0.058	0.176

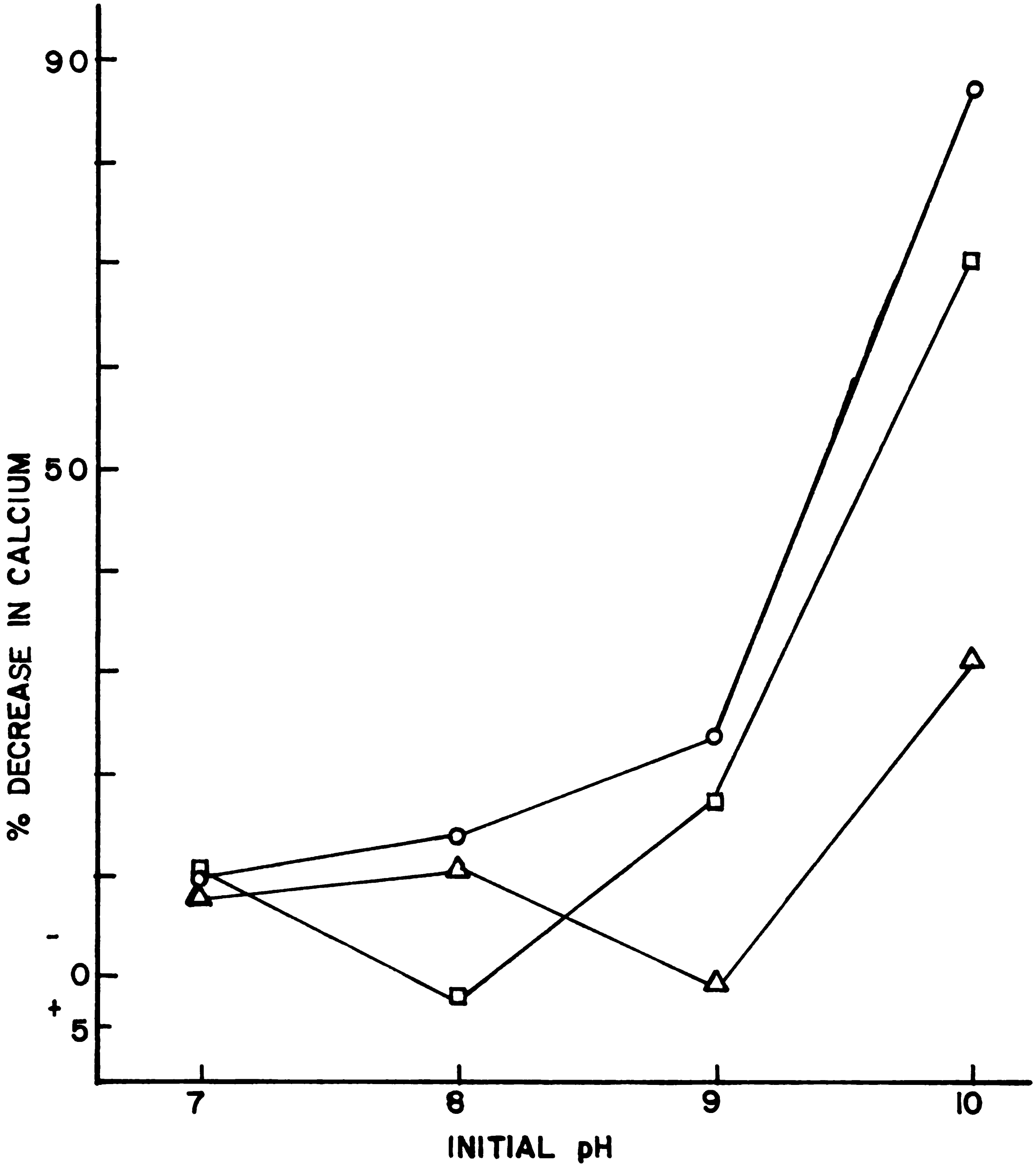
words, alkalinity, for example, was measured twice on one given initial pH value. Phosphorus, however, is the average of only two values: one from each flask for either ortho or total phosphorus.

The intense relationship between pH and alkalinity needs no explanation. The range of initial pH values do represent naturally occurring levels, but no reduction in alkalinity occurs naturally until ions are removed from solution by precipitation -- usually as $CaCO_3$ in the range of pH 8.3 to 11. Using a mineral acid to adjust initial pH, as was done in these experiments, consumes the amount of alkalinity resisting pH change. Unfortunately, the volume of acid added was not measured and quantification of actual changes in alkalinity, due to either pH adjustment or treatment, cannot be obtained.

Differences between experiments reflect the initial alkalinity of the treated water. Recarbonation, as seen in the 48-hour pH values, shows as a decrease in the pH toward an equilibrium value near the pre-treatment pH. The higher concentration of hydroxyl ion at upper pH values, especially 10.0, neutralize the carbonic acid dissociations.

Calcium exhibits a distinct decrease as the adjusted pH is increased (Figure 1). The minimum solubility of $CaCO_3$ occurs near pH 8.4 and also corresponds with its zero point of charge (ZPC), indicating it is readily coagulated at this pH (Stumm and Morgan, 1970). At pH values greater than 8.4, Ca^{+2} is increasingly associated with carbonates, hydroxyapatite and, to a lesser extent, bicarbonate. The formation of calcium carbonate precludes formation of phosphate compounds, but the calcite crystal does serve as a heterogeneous

Figure 1. Percent decrease in calcium 48 hours after initial pH adjustment for pH controls in Exp. I (○), Exp. II (□) and Exp. III (△).


90
50
-
0
+
5
% DECREASE IN CALCIUM
7
8
9
10
INITIAL pH

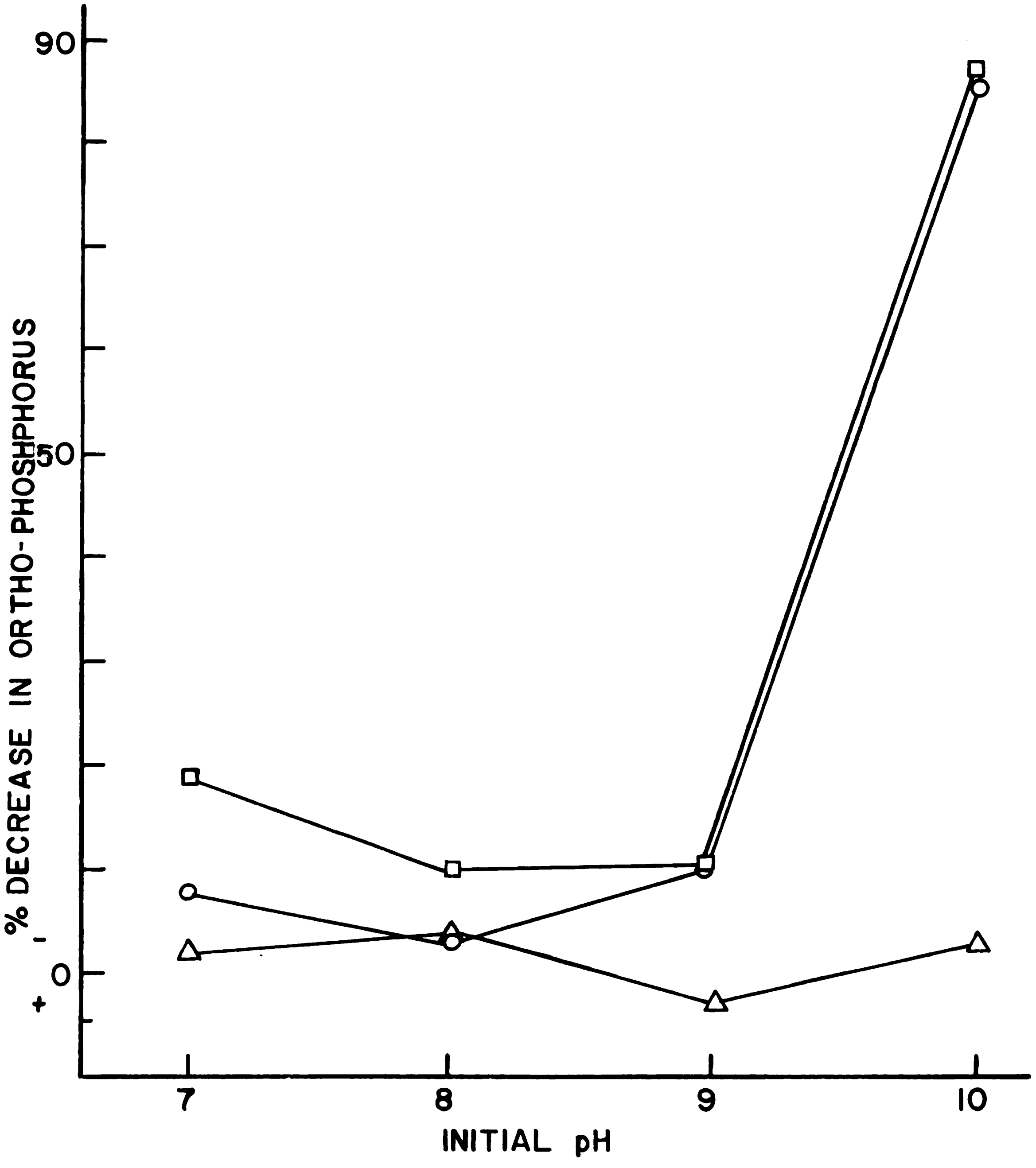
nucleation site which facilitates faster apatite formation. Relatedly, phosphate does co-precipitate with calcite (Otsuki and Wetzel, 1972) and may further expedite hydroxyapatite formation.

Opposing this phosphate removing reaction is the organic matter which "poisons" crystal formation (Bachra _et_ _al_., 1963). Similarly, Simkiss (1964) reported that HCO_3^- interferes with the precipitation of apatite, while HOP_4^- interferes with calcite precipitation (no mention of co-precipitation was made). The presence of both anions results in a substance with a crystalline structure somewhere between calcite and hydroxyapatite, depending upon the amount of anion interference. Nonetheless, as reported by Leckie and Stumm (1970) and in Figures 1 and 2, calcium and phosphate are still removed from solution as the pH is raised.

Concomitant with the foregoing removal mechanism is a postulated second method indirectly seen in the presented data. The presence of indigenous organic, exocellular polymers may be augmenting the calcium-phosphate-hydroxyl mechanism (King, 1975).

Pavoni _et_ _al_. (1971, 1972) have shown effective removal of kaolinite (inorganic clay colloid) suspensions from solution with extracted algal and bacterial exocellular polymers. Optimum removal occurred at pH 11.0 with marked decreases in solution turbidity beginning near pH 8. Therefore, removal is highly dependent upon the pH of the colloid solution. The increasing concentration of the potential determining hydroxyl ion (OH^-) leads to a negative surface potential and a repulsion of the negatively charged polymers might be expected, but such is not the case. Indeed, the surface potential is negative, but bioflocculation, and presumably the involved polymers,

Figure 2. The percent decrease in orthophosphate 48 hours after initial pH adjustment for pH controls in Exp. I (○), Exp. II (□) and Exp. III (△).


% DECREASE IN ORTHO-PHOSPHORUS
90
50
-
0
+
7
8
9
10
INITIAL pH

requires no reduction in surface potential before bridging by physical and electrostatic bonding can occur (Stumm and Morgan, 1970; Pavoni et al., 1971, 1972).

Figure 2 dipicts the percent decrease, or removal, of phosphate from the pH control flasks for the three experiments. Removal in Exp. I and Exp. II is similar, in that approximately 85% of the orthophosphate was removed at pH 10.0. This corresponds well with the results of Pavoni and co-workers (1971, 1972). Exp. III, on the other hand, shows a net removal at pH 10.0 of only 3.1% of the original orthophosphate present. Water for Exp. III was obtained from Pond 2, and may have contained less exocellular polymer, therefore, less phosphate was flocculated and removed by pH adjustment. Assuming this hypothesis is accepted, two mechanisms are operating to remove phosphate; calcite-hydroxyapatite formation and polymer flocculation. Further evidence for the latter will be presented.

Calcium decreased 31% at pH 10.0 in Exp. III, 71% in Exp. II, and 87% in Exp. I (Figure 1) and it appears that calcium and phosphate removal (Figure 2) are related to the pH of the solution, which it is. However, this does not mean that calcium phosphate compounds are precipitated directly. What it does imply is that phosphate and hydroxide are complexing with the calcium to form a colloidal suspension which is subsequently removed by the exocellular polymer.

Solubility products predict the presence of $CaHPO_4$, $Ca\ H(PO_4)_3$ and $Ca_{10}(PO_4)_6(OH)_2$ (Leckie and Stumm, 1970; Stumm and Morgan, 1970) between pH 8 and pH 10. These complexes do form regardless of polymer concentration. Should sufficient quantity of polymer exist to coagulate the calcium-phosphate complexes, simply raising the pH would promote bridging and effect their removal. In the absence of polymers, calcium-phosphate complexing still occurs, but raising the pH would do little except precipitate a small amount of calcite. Recalling the mutual interferences of HPO_4^- and HCO_3^- in calcite and hydroxyapatite formation (Bachra _et_ _al_., 1963; Simkiss, 1964), indigenous organic polymers take on the role of calcium-phosphate complex removing stimuli in that they increase the rate of removal despite anion interference.

In Exp. III, calcium is interacting with solution phosphate and remaining as a colloidal dispersion. Adjusting the pH removed little phosphate or calcium. Not until a treatment of aluminum, calcium sulfate or their combination was added did a significant removal of phosphate (85 to 89%) or calcium (50 to 55%) occur (Table 5). Therefore, removal was not effected until a flocculant was added, a requirement apparently fulfilled by indigenous exocellular polymers in Exp. I and Exp. II.

The foregoing conclusions are _a_ _priori_ and cannot be rigorously substantiated with the present data; therefore, future research may consider this hypothesis worthy of investigation.

Total phosphorus data are presented, but major emphasis is placed upon the total particulate orthophosphorus form for two reasons: (1) Soluble ortho-P is the most readily assimilated nutrient source; and (2) The majority of the total phosphorus measured was in the ortho-form (_viz_. Exp. I 90%; Exp. II 80%; and Exp. III 83%). Soluble ortho-P was not measured, but would have indicated by difference, the amount of phosphorus associated with complexes as well as that which is not complexed.

Table 5. Percent change (%Δ) in calcium and orthophosphate 48 hours after treatment in Exp. III. + = increase and no sign = decrease.

Treatment	Observation (in mg/l)	Adjusted pH			
		7.0	8.0	9.0	10.0
pH adjustment	%Δ Ca	7.9	10.3	+0.5	31.2
	%Δ P	1.6	3.1	+3.1	3.1
Combined (12.3 mg $CaSO_4$/l + 0.43 mg Al/l)	%Δ Ca	+10.4	0.7	+6.4	55.6
	%Δ P	4.3	2.3	+2.3	89.1
$CaSO_4$ (12.3 mg/l)	%Δ Ca		+9.3		51.2
	%Δ P		2.3		85.2
Aluminum (0.43 mg/l)	%Δ Ca		9.2		43.2
	%Δ P		4.3		89.4

Trends in the total-P usually followed those of the ortho-P; however, several large, unexplained increases in total-P were observed. They have been attributed to experimental error and variation in digestion efficiency. The latter is not unreasonable considering the water source and its possible refractory constituents.

Effect of Calcium Sulfate Treatment

The application of calcium sulfate did produce changes over and above those caused by pH adjustment and may be noted by comparing Table 4 with Table 6 (initial values are listed in Table 3).

After 48 hours, alkalinity showed very little variation from pre-treatment values in Exp. I except at pH 10.0. Here, the decrease represents that lost to precipitation or complexation as seen in the pH control units. Exp. II and III showed changes closely paralleling those of the pH control units and may be attributed to pH adjustment. No explanation is readily offered for the apparently unchanging alkalinity values of Exp. I.

The pH, like alkalinity, paralleled, and sometimes equalled, the values recorded for the pH controls. Therefore, increasing the calcium sulfate dosage from 12.3 mg/l to 35 mg/l did not have an effect on pH or alkalinity that could be separated from the effects of pH adjustment.

At the temperature and pH values encountered in natural waters, calcium sulfate is reasonably insoluble and tends to settle rapidly through the water column in an aggregated mass. Despite attempted dissolving prior to addition, the majority of the $CaSO_4$ settled to the bottom of the flask regardless of pH. Only after 48 hours were

Table 6. Effect of calcium sulfate on five parameters 48 hours after treatment in three experiments: Exp. I, 25 mg/l; Exp. II, 35 mg/l; and Exp. III, 12.3 mg/l.

	Initial pH											
	7.0			8.0			9.0			10.0		
Parameter	I	II	III	I	II	III	I	II	III	I	II	III
$CaSO_4$												
Alkalinity (meq/l)	2.2	2.4		2.2	2.9	1.7	2.1	2.8		1.6	2.7	1.8
pH	7.2	7.4		7.4	8.2	7.9	7.8	8.9		9.3	10.2	10.0
Calcium (mg/l)	72.0	90.8		61.3	78.4	63.8	47.6	53.4		6.9	21.6	28.5
Ortho-P (mg/l)	0.239	0.286		0.236	0.291	0.125	0.206	0.325		0.014	0.020	0.122
Total-P (mg/l)	0.264	0.356		0.278	0.356	0.180	0.250	0.314		0.033	0.058	0.170

the aggregates dissolved. Ignoring this insolubility, it is assumed that all of the calcium present is available for complexing or precipitation when $CaSO_4$ is added. Therefore, Table 7 cites the total Ca^{+2} concentrations in each experiment immediately following $CaSO_4$ additions; for it is these values which are used in calculating the percent change in calcium shown in Figure 3.

Here, as in Figure 1, there is a distinct decrease (increased removal) in calcium with increasing pH. A similar removal is shown in Figure 4 where $CaSO_4$ treatment increased orthophosphate removal by 10% over the pH controls. Increasing the $CaSO_4$ dosage from 12.3 mg/l to 35 mg/l resulted in only slight (ca. 12%) improvements in phosphate removal at the lower pH levels of each experiment except Exp. III (Table 5).

Removal of phosphate with 12.3 mg/l of $CaSO_4$ (Exp. III) was negligible at pH 8.0, but increased significantly at pH 10.0 (Figure 7) for reasons explained previously.

Combining aluminum with calcium sulfate (Exp. III) removed little more phosphate at pH 7.0, 8.0 and 9.0 than the individual treatments accomplished at pH 8.0 (Table 5). Absence of exocellular polymers may be the cause for the lower removal. At pH 10.0, phosphate removal is identical for each treatment as well as for the combination, suggesting no advantage is gained, over 48 hours, by combining the two compounds (Figure 5). Given the choice between calcium sulfate and aluminum for treatment of a lake at any pH, aluminum is the best choice as will be seen in the following section.

In general summary thus far, the majority of change in a single parameter in the three experiments can be attributed to adjusting the

Table 7. Calcium concentrations before treatment (initial), the amount added and the amount assumed to be available for phosphate removal immediately following addition of calcium sulfate for three experiments.

	Calcium (mg/l)		
Experiment	Initial	Added	Total
I	64.60	4.31	68.91
II	72.80	6.03	78.83
III	58.40	2.12	60.52

Figure 3. Percent decrease in calcium 48 hours after treatment with calcium sulfate at three levels: Exp. I, 25 mg/l (○); Exp. II, 35 mg/l (□); and Exp. III, 12.3 mg/l (△, only two points).

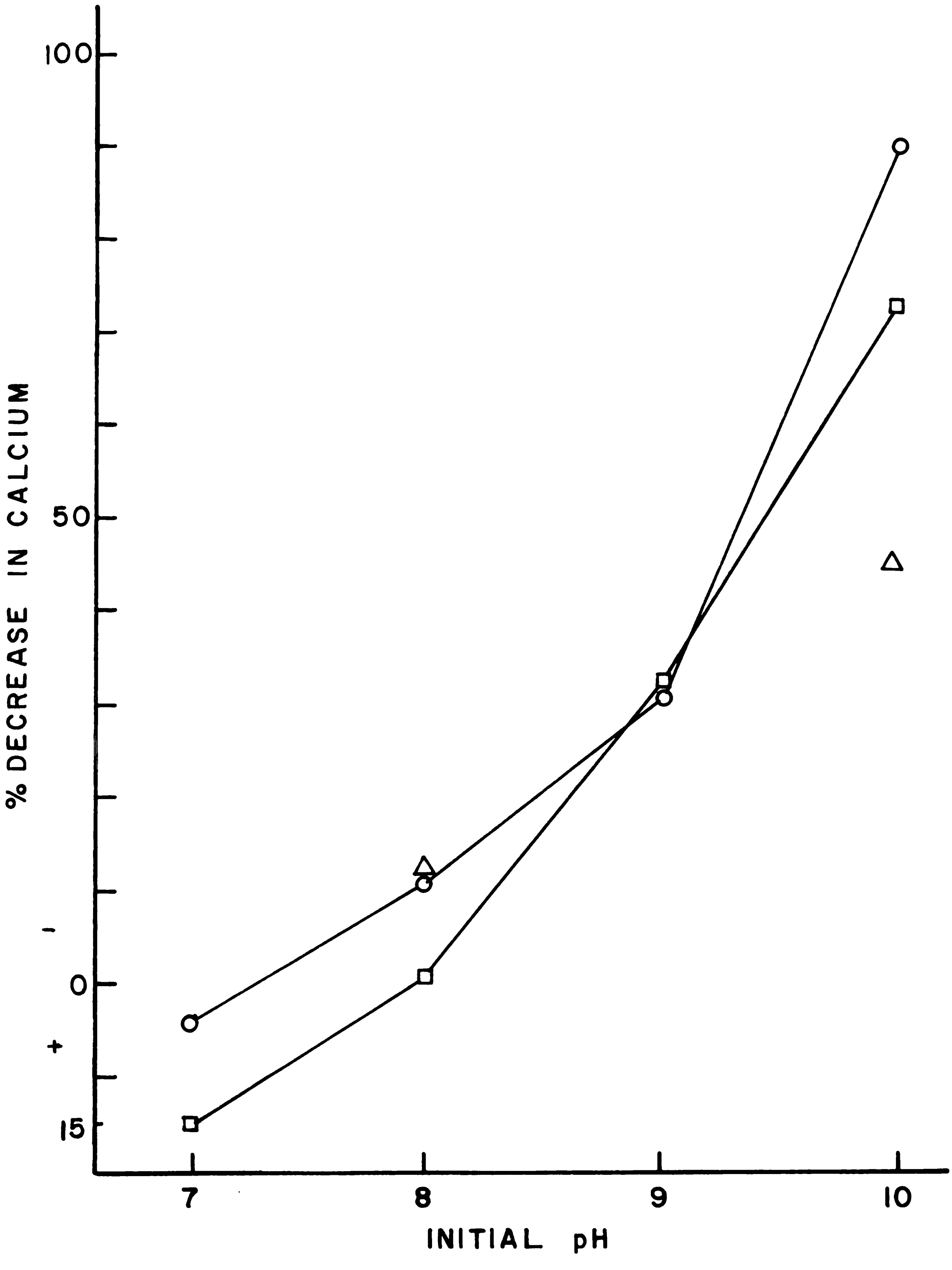
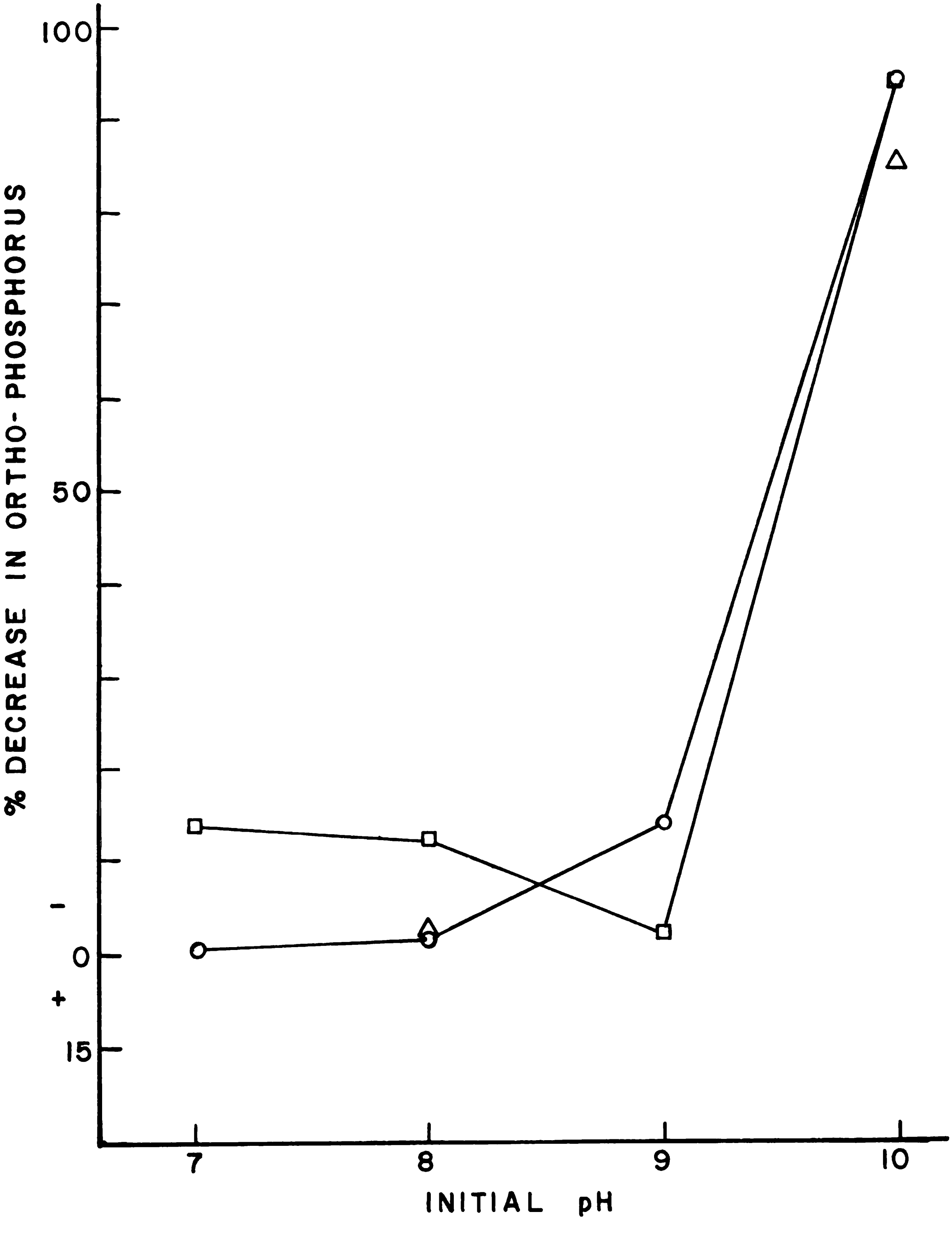
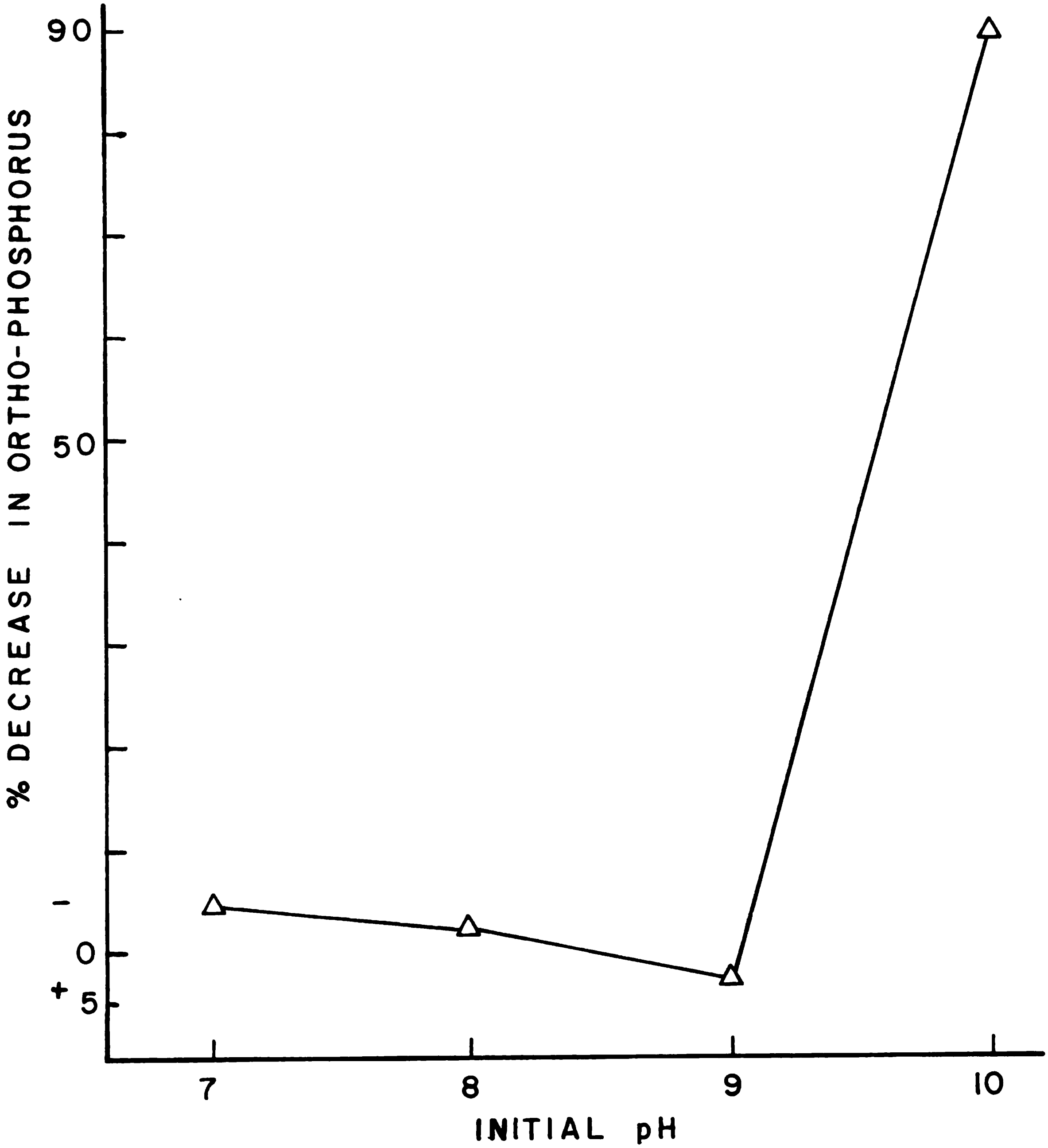

% DECREASE IN CALCIUM
100
50
0
15
-
+
7
8
9
10
INITIAL pH

Figure 4. Percent decrease in orthophosphate 48 hours after treatment with calcium sulfate at three levels: Exp. I, 25 mg/l (○); Exp. II, 35 mg/l (□); and Exp. III, 12.3 mg/l (△ ; only two points).



% DECREASE IN ORTHO- PHOSPHORUS
100
50
-
0
+
15
7
8
9
10
INITIAL pH

Figure 5. Percent decrease in orthophosphate 48 hours after treatment with a combined treatment of calcium sulfate (12.3 mg/l) and aluminum (0.43 mg/l).



90
50
–
0
+ 5
% DECREASE IN ORTHO-PHOSPHORUS
7
8
9
10
INITIAL pH

pH prior to treatment. Calcium sulfate, by itself, has little phosphorus removing capability within 48 hours. Upon application of $CaSO_4$ to a lake, it would aggregate due to its low solubility and settle rapidly through the water column. In this form it could, at best, provide agglomeration or adsorption sites for suitable ions.

Effect of Aluminum Treatment

Upon addition of the alum to each flask, the water became cloudy with a visible floc forming within 1 to 2 minutes after stirring was stopped. In Exp. I (20 mg Al/l), the floc tended to float at the surface due to air bubbles entrapped along with color contributing substances presumed to be algae, suspended particles and dissolved color producing compounds. After 36 hours the surface layer of floc had not settled, but the bottom of the flask was covered with that floc which had passed through the water column. Stirring the upper few cm. dispersed the surface floc and it subsequently settled.

In Exp. II (15 mg Al/l), the floc was less abundant, but still floated at the surface; immediate stirring facilitated settling.
No visible floc was formed in either the combined or individual treatment units of Exp. III (0.43 mg Al/l).

The settled material of pH 10.0 flasks in all three experiments was characteristically a coarse, white substance (presumably carbonates) which had to be scraped from the bottom of the flask. Accumulation of this material in Exp. III was much slower and less abundant than in the previous experiments.

In pH 9.0 flasks, some of this type of material appeared, but the majority of the bottom matter was similar to that of pH 8.0 and 7.0

flasks: a fluffy, greenish-grey to greenish-white amorphous substance. No mass or volume quantification of this material was attempted.

An increase in the quantity of floc formed increases with increasing doses of alum (Peterson et al., 1973). This has practical considerations because field applications of alum are usually characterized by floc floating at the surface, collecting in the emergent vegetation and thereby decreasing phosphate removal from the limnetic photic zone. Besides decreasing the treatment level to avoid surface accumulations, subsurface injection of the alum slurry is being tested (Cooke, 1974).

Results of aluminum treatment are presented in Table 8; comparison with Table 3 will show several definitive changes due to the treatment.

The hydrolysis of aluminum produces a decrease in alkalinity and pH by binding OH^-. This disrupts the carbonate-bicarbonate-hydroxyl balance shifting it toward bicarbonate-carbonic acid associations. From the data, alkalinity was maximally reduced at the lowest initial pH of the highest treatment level (Exp. I); pH also reached its lowest post-treatment value (5.8). As the initial pH increased, the amount of alkalinity consumed decreased due to direct Al^{+3}-OH^- interaction; especially at pH 10.0. Differences between experiments reflect both initial alkalinity concentrations (Table 3) and decreasing dosages of aluminum.

Decreases in pH below recarbonation levels, as also seen in the pH controls, is due to aluminum hydrolysis and is also a function of aluminum dosage. The tendency for pH to decrease to near 6.0 suggests

Table 8. Effect of aluminum sulfate on five parameters 48 hours after treatment in three experiments: Exp. I, 20 mg Al/l; Exp. II, 15 mg Al/l; and Exp. III, 0.43 mg Al/l.

	Adjusted pH											
	7.0			8.0			9.0			10.0		
Parameter	I	II	III	I	II	III	I	II	III	I	II	III
Alkalinity (meq/l)	0.5	1.0		0.7	1.5	1.7	1.4	2.2		2.1	3.2	1.5
pH	5.8	6.8		6.2	7.0	7.9	6.8	7.4		8.2	9.1	9.6
Calcium (mg/l)	65.0	78.2		63.0	69.9	53.1	65.8	76.4		44.9	38.6	33.2
Ortho-P (mg/l)	0.002	0.000		0.004	0.000	0.122	0.002	0.000		0.008	0.023	0.019
Total-P (mg/l)	0.006	0.013		0.010	0.006	0.179	0.008	0.008		0.022	0.058	0.056

favorable conditions for precipitation of $AlPO_4$ which is maximum in this range. Aluminum phosphate precipitation becomes less important as the initial pH increases to 10.0 and pH depressions due to treatment become smaller.

Because aluminum is toxic to plankton and trout (Peterson et al., 1973; Kennedy and Cooke, 1974), precautions are necessary to prevent high concentrations of residual Al^{+3} in solution. These result when alum doses exceed the buffer capacity of the treated water and essentially consume the alkalinity. Kennedy and Cooke (1974) have shown that a 20 mg Al/l dosage removed 96% of the initial alkalinity (2.0 meq/l); no pH was given. Preliminary studies and final data on Horseshoe Lake showed similar decreases in alkalinity and pH after treatment was applied (Peterson et al., 1973).

Calcium values changed very little within each experiment except at pH 10.0 (Figure 6) as was expected and discussed above. This lack of change in the presence of aluminum suggests an interesting explanation when the phosphorus data is also conferred, as is done below.

Orthophosphate was significantly removed (Figure 7) with the larger alum doses of Exp. I and Exp. II through hydroxy-aluminum complexes adsorbing and/or absorbing the phosphate. This interaction, besides removing the phosphate present, significantly reduced the concentration of hydroxide ion (decreased pH) and precludes the Ca-OH-PO_4 complexing interaction at the lower three pH levels. At pH 10.0, however, carbonate and hydroxide remaining in solution could remove the calcium present. Therefore, the change in calcium would be minimal at the lower pH values and increase at pH 10.0, which is observed in Table 8 and Figure 6.

Figure 6. Percent decrease in calcium 48 hours after treatment with aluminum at three levels: Exp. I, 20 mg/l (○); Exp. II, 15 mg/l (□); and Exp. III, 0.43 mg/l (△) at two pH values.

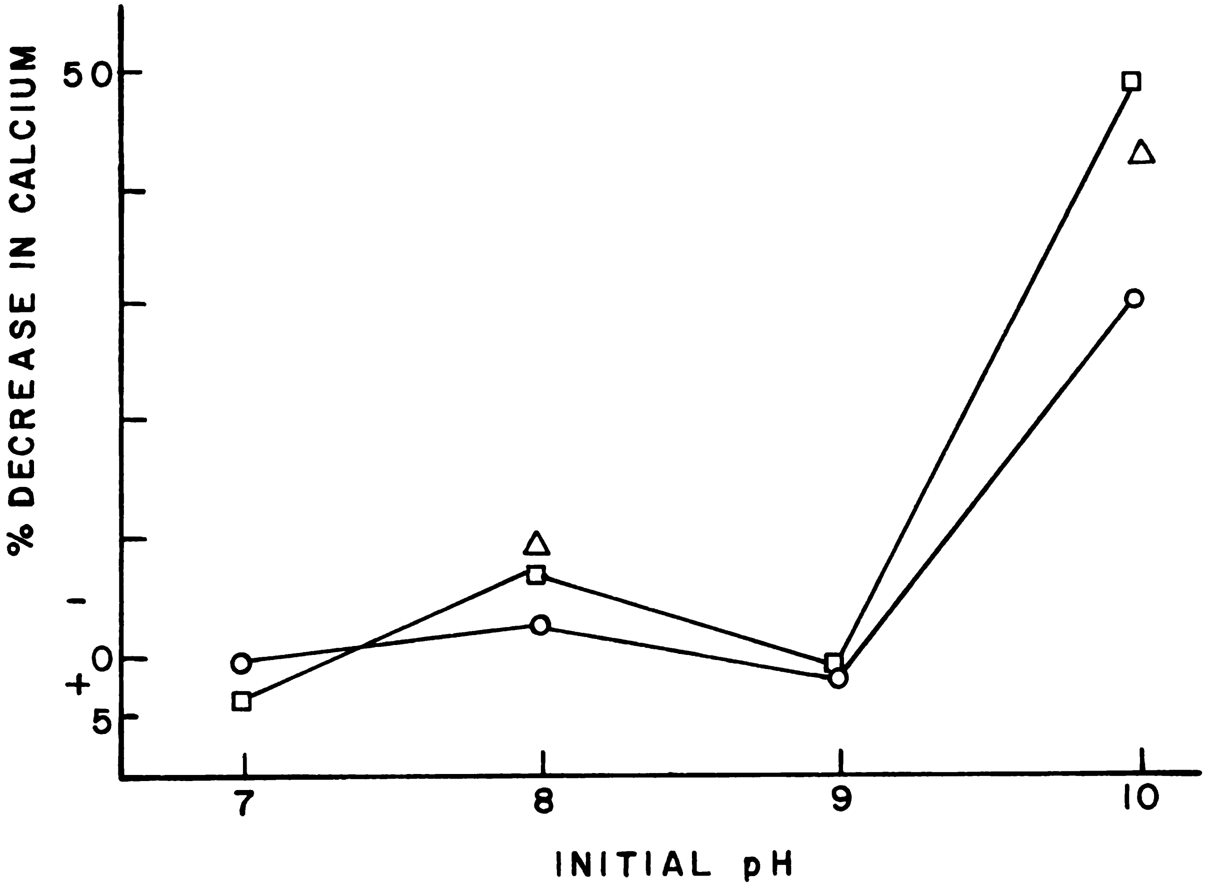
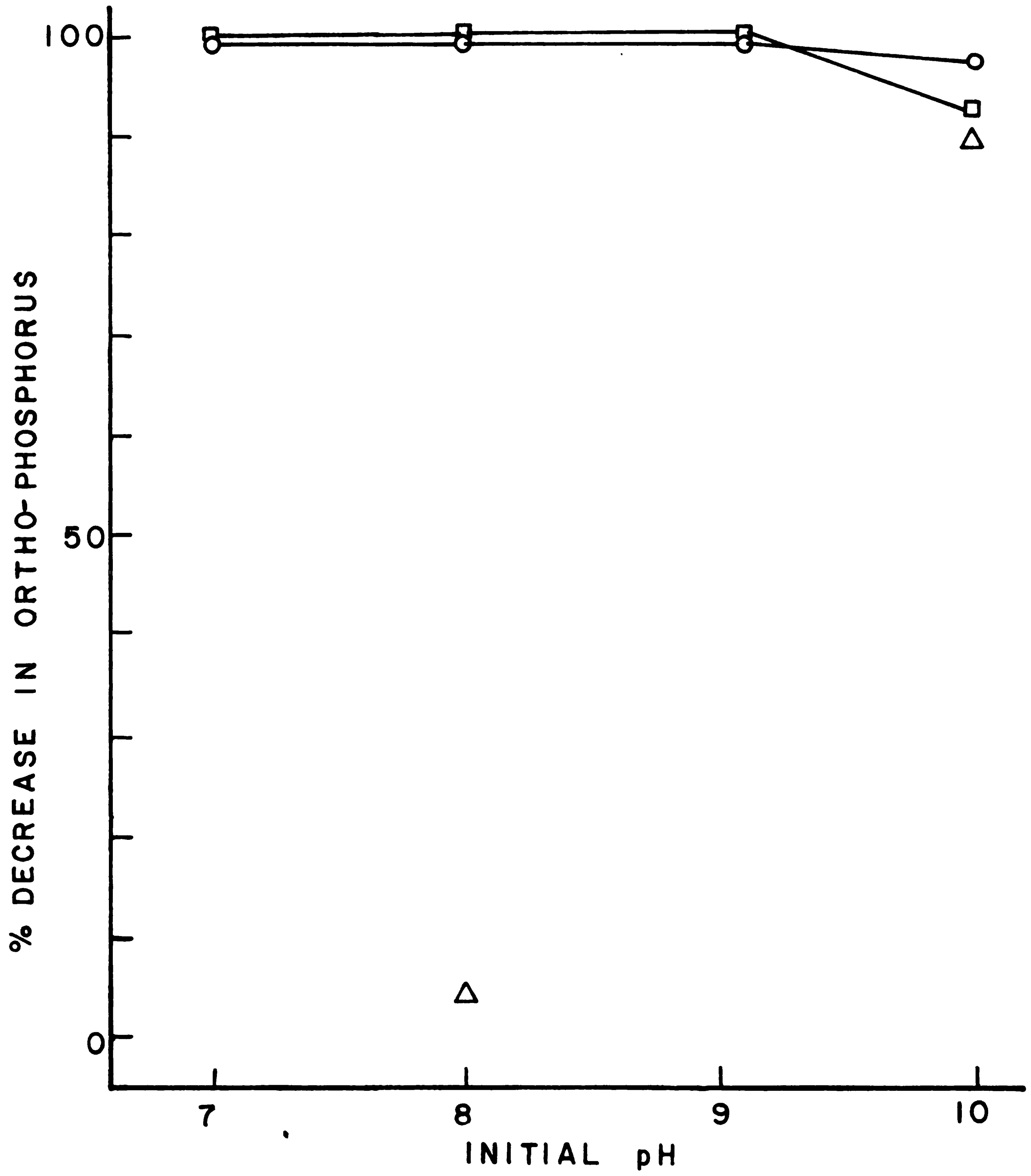

% DECREASE IN CALCIUM
50
-
+0
5
7
8
9
10
INITIAL pH

Figure 7. Percent decrease in orthophosphate 48 hours after treatment with aluminum at three levels: Exp. I, 20 mg/l (○); Exp. II, 15 mg/l (□); and Exp. III, 0.43 mg/l (△) at two pH values.


100
50
0
% DECREASE IN ORTHO-PHOSPHORUS
7
8
9
10
INITIAL pH

Increasing the aluminum dosage from 0.43 mg/l to 15 mg/l facilitated complete orthophosphate removal while raising the concentration to 20 mg/l accrued no additional reduction. Treatment with 0.43 mg/l is ineffective in removing P from solution unless the pH is increased to 10.0, where $CaSO_4$ is just as effective (Table 5).

The possible role of aluminum in the combined treatment was presented above, but it is instructive to note that in these units of Exp. III (Table 9), alkalinity, calcium and pH approximated the 48 hour values of the pH controls while phosphate was slightly lower (Table 4). This is further indication that the low concentrations of aluminum and/or calcium sulfate were insufficient for effective phosphate removal.

It is conceivable that adding $CaSO_4$ and aluminum in combination to a lake is designed to increase Ca-PO_4 complexing and colloid formation. At the treatment pH of the lake, usually less than pH 9.0, aluminum could remove the formed colloids if it were present in sufficient quantity to destabilize them. But it is more likely that $CaSO_4$, due to its low solubility, settles rapidly out of the water column and dissolves slowly, if at all, on the sediment-water interface. Thus, aluminum becomes the active and main ingredient for effective phosphate removal.

Table 9. Percent change (%Δ) in orthophosphate and calcium 48 hours after treatment with a combination of 12.3 mg $CaSO_4$/l and 0.43 mg Al/l. + = increase; no sign = decrease.

Observation (in mg/l)	Adjusted pH 7.0	8.0	9.0	10.0
%Δ Ca	+10.4	0.7	+6.4	55.6
%Δ P	4.3	2.3	+2.3	89.1

SUMMARY

Adjusting pH had a substantial effect on the measured parameters. Besides decreasing the alkalinity by one meq/l initially, after 48 hours the pH decreased toward 7.0 due to recarbonation while calcium changed very little until pH 10.0 where decreases of 87 and 71% respectively, were observed in Exp. I and Exp. II. Calcium in Exp. III did not follow this trend due to the postulated absence of exocellular polymers of algae and bacteria. Phosphate removal was on the order of 85% after 48 hours.

Treatment with calcium sulfate showed no apparent effect that could be distinguished from that of adjusting the pH prior to treatment. As a phosphate removing agent, calcium sulfate functioned insignificantly within the observed 48 hours.

Aluminum, however, was equally effective at the two higher doses (20 mg/l and 15 mg/l), suggesting the lower dosage most economical for P-removal. Alkalinity and pH were substantially reduced by the higher doses, but calcium was unaffected until the initial pH was raised to 10.0.

Exp. III is viewed as a special case in that: a. aluminum added was very low; b. no significant P-removal was incurred by raising the pH as was the case in the previous experiments; c. alum induced a P-removal similar to that of $CaSO_4$ at pH 10.0 whether added separately or in combination. The absence of exocellular polymer is hypothesized.

The application of a combined treatment in an 80% $CaSO_4$:20% alum proportion showed effects similar to those seen in the pH controls. The alum is concluded to be the active phosphate removing ingredient at typical pH levels (7 to 9) encountered in lakes to be treated.

CONCLUSIONS

For levels of phosphate present, aluminum was the most effective treatment for its removal when applied in concentrations bracketing the level frequently used in actual lake treatment (18 mg/l). No increased P-removal was achieved by using 20 mg Al/l compared to removal with 15 mg Al/l.

The effectiveness of calcium sulfate was determined more by the pH adjustment than by its dosage and, as such, is a poor choice for lake treatment.

Combining the two salts in a proportion of 80% $CaSO_4$ and 20% alum was ineffective in removing phosphate at pH 8.0, the point at which this combined treatment is usually applied to a lake. Several factors may have entered in: 1) insufficient amounts of aluminum were available; 2) phosphate levels were too high; or 3) the absence of biological exocellular polymers prohibited removal. While these apply mainly to the foregoing research, a field application would be subject to similar circumstances of uncertainty. To avoid this, it is suggested that an alum treatment of 15 to 18 mg/l be used to assure phosphate removal. This will also be possible at a lower cost. Judicious application will preclude any potential toxicity.

While lake rehabilitation is a therapeutic treatment seeking to undo damage incurred; it is not a substitute for reducing allochthanous nutrient loading to a lake by wise drainage basin management.

LITERATURE CITED

LITERATURE CITED

Bachra, B. N., O. R. Trautz and S. L. Simon. 1963. Precipitation of calcium carbonates and phosphates. Arch. Biochem. and Biophysics 103: 124-138.

Browman, M. G., R. F. Harris and D. E. Armstrong. 1973. Unpublished report.

Clesceri, N. 1968. Physical and chemical removal of nutrients. *in* Algae, Man and the Environment ed. by D. F. Jackson. Syracuse University Press. 454 pp.

Cooke, G. D. 1974. Department of Biological Sciences and Center for Urban Regionalism and Environmental Systems; Kent State University; Kent, Ohio. Personal communication.

Ferguson, J. F., D. Jenkins and J. Eastmen. 1973. Calcium phosphate precipitation at slightly alkaline pH values. Jour. Water Poll. Control Fed. 45(4): 620-631.

Jenkins, D., J. F. Ferguson and A. B. Menar. 1971. Chemical processes for phosphate removal. Water Research, Vol. 5. Pergamon Press, England. pp. 369-389.

Kennedy, R. H. and G. D. Cooke. 1974. Unpublished manuscript.

King, D. 1975. Department of Fisheries and Wildlife; Michigan State University; East Lansing, Michigan. Personal communication.

Lainge, R. L. 1974. A non-toxic lake management program. Hyacinth Control Jour. 12: 41-43.

Leckie, J. and W. Stumm. 1970. Phosphate precipitation. *in* Water Quality Improvement by Physical and Chemical Methods. III. Ed. by E. F. Gloyna and W. W. Eckenfelder. Univ. Texas Press, Austin, Texas. pp. 237-249.

Malhotra, S. K., G. F. Lee and G. A. Rolich. 1964. Nutrient removal from secondary effluent by alum flocculation and lime precipitation. Inter. Jour. Air and Water Poll., Vol. 8. Pergamon Press, England. pp. 487-500.

Olphen, H. van. 1963. An introduction to clay colloid chemistry. Wiley-Interscience, New York. As cited in Stumm and Morgan, 1970.

O'Melia, C. R. and W. Stumm. 1967. Aggregation of silica dispersions by iron (III). Jour. Colloid and Interface Sci. 23: 437-447.

O'Melia, C. R. 1969. A review of the coagulation process. Public Works. May: 87-98.

Otsuki, A. and R. G. Wetzel. 1972. Coprecipitation of phosphate with carbonates in a marl lake. Limnol. Oceanogr. 17: 763-767.

Pavoni, J. L., M. W. Tenney and W. F. Echelberger, Jr. 1971. The relationship of algal exocellular polymers to biological flocculation. *in* Engineering Bulletin of Purdue Univ. Proceedings of the Twenty-sixth Industrial Waste Conference, May, 1971. Engineering Extension Series #140, Pt. II. pp. 957-974.

Pavoni, J. L., M. W. Tenney and W. F. Echelberger, Jr. 1972. Bacterial exocellular polymers and biological flocculation. Jour. Water Poll. Control Fed. 44(3): 414-431.

Peterson, J. P., J. P. Wall, T. L. Wirth and S. M. Born. 1973. Eutrophication control: nutrient inactivation by chemical precipitation at Horseshoe Lake, Wisconsin. Tech. Bull. #62. Wisconsin Department of Natural Resources. Madison, Wis. 19 pp.

Sillen, L. G. and A. E. Martell. 1964. Stability constants of metal-ion complexes. Special Publication, No. 17. The Chemical Society, London.

Simkiss, K. 1964. Phosphates as crystal poisons of clacification. Biol. Rev. 39: 487-505.

Standard Methods for the Examination of Water and Wastewater. 1973. 13th edition. Published jointly by the American Public Health Association, American Water Works Association and the Water Pollution Control Federation. Washington, D. C. 874 pp.

Stumm, W. and J. J. Morgan. 1962. Chemical aspects of coagulation. Jour. Amer. Water Works Assoc. 54: 971-992.

Stumm, W. and J. J. Morgan. 1970. Aquatic chemistry. Wiley-Interscience, New York. 583 pp.

Wetzel, R. G. 1975. Limnology. W. B. Saunders, Co., Philadelphia. In press.

Yuan, W. L. and P. H. Hsu. 1971. Effect of foreign components on the precipitation of phosphate by aluminum. *in* Advances in Water Pollution Research, the Fifth International Conference. Vol. I. Pergamon Press, England. pp. I-16/1 to I-16/12.